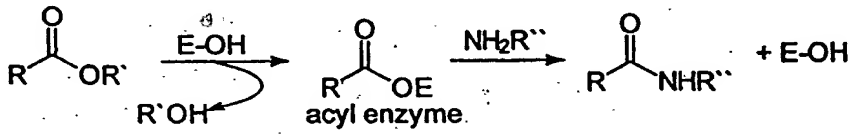
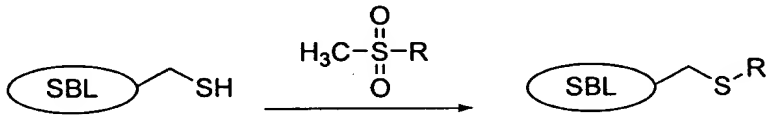


Figure 1

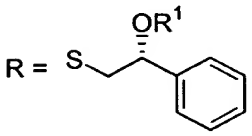
Fig. 1

Scheme 1. Modification of SBL mutants with Chiral Auxiliaries.

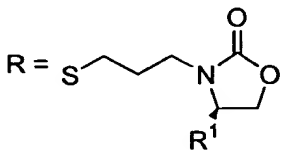


1a - i

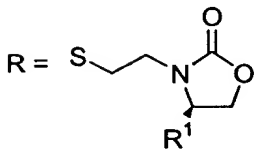
Diastereomeric Enzyme
R = (*R*) or (*S*) modifier



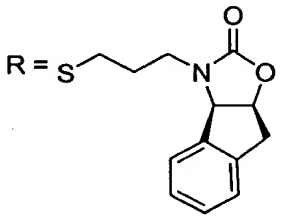
(*R*)-**a** R^1 = Me
(*R*)-**b** R^1 = H



c R^1 = H
(*R*)-**d** R^1 = *i*Pr
(*R*)-**e** R^1 = Ph
(*R*)-**f** R^1 = Bn



(*R*)-**g** R^1 = Ph
(*R*)-**h** R^1 = Bn

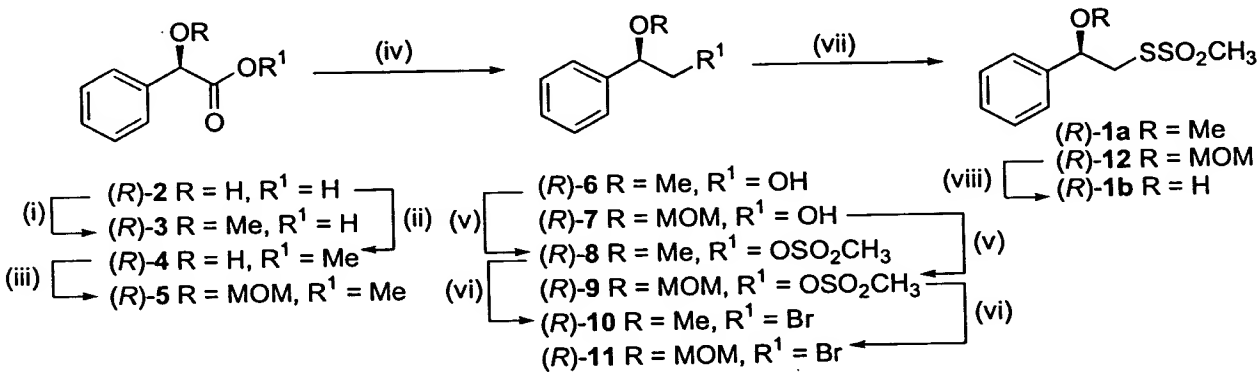


(*R*)-**i**

The corresponding (*S*) MTS ligands follow the same code scheme (i.e. (*S*)-**a**, (*S*)-**b**, (*S*)-**d**, (*S*)-**e**, (*S*)-**f**, (*S*)-**g**, (*S*)-**h**, (*S*)-**i**).

Fig. 2

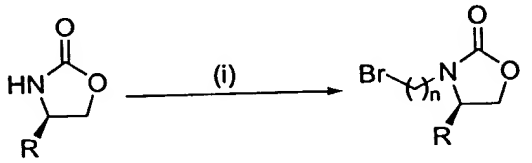
Scheme 2. Synthesis of Mandelate-based Ligands



Reagents: (i) Me_2SO_4, NaOH, H_2O, 37%; (ii) MeOH, H^+; (ii) MOM-Cl, CH_2Cl_2, Et_3N (90% 2 steps); (iv) For (*R*)-**3**: BH_3, THF, 82%; For (*R*)-**5**: $LiBH_4$, THF, 97%; (v) $MeSO_2Cl$, CH_2Cl_2, Et_3N; For (*R*)-**8**: 100%; (vi) LiBr, acetone; For (*R*)-**10**: 84%; For (*R*)-**11**: 78% 2 steps; (vii) $NaSSO_2CH_3$, DMF; For (*R*)-**12**: 61%; (viii) TFA, H_2O, 82%.

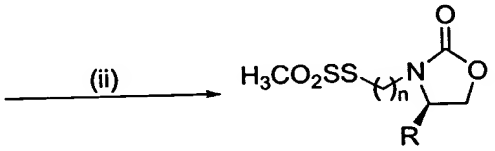
Fig. 3

Scheme 3. Synthesis of Oxazolidinone-based Ligands



13 R = H
(*R*)-**14** R = *i*Pr
(*R*)-**15** R = Ph
(*R*)-**16** R = Bn

17 R = H, n = 3
(*R*)-**18** R = *i*Pr, n = 3
(*R*)-**19** R = Ph, n = 3
(*R*)-**20** R = Bn, n = 3
(*R*)-**21** R = Ph, n = 2
(*R*)-**22** R = Bn, n = 2

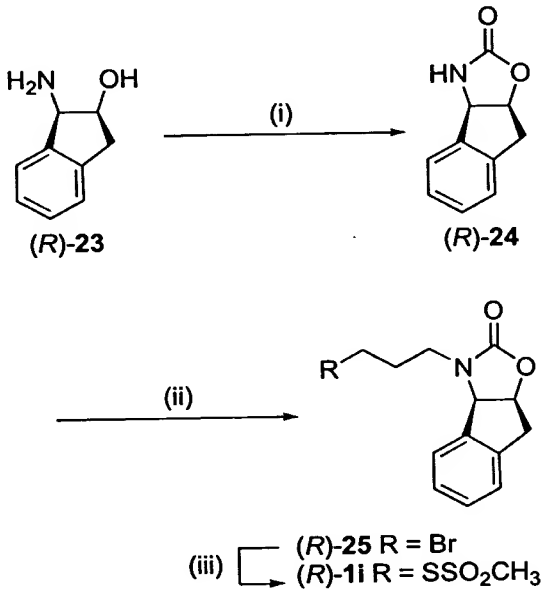


1c R = H, n = 3
(*R*)-**1d** R = *i*Pr, n = 3
(*R*)-**1e** R = Ph, n = 3
(*R*)-**1f** R = Bn, n = 3
(*R*)-**1g** R = Ph, n = 2
(*R*)-**1h** R = Bn, n = 2

Reagents: (i) KOH, DMSO, Br $(CH_2)_nBr$;
(ii) $NaSSo_2CH_3$, DMF.

Fig. 4

Scheme 4. Synthesis of Indanol-based Ligands



Reagents: (i) triphosgene, CH_2Cl_2, Et_3N, 100%; (ii) KOH, DMSO, $Br(CH_2)_3Br$; (iii) $NaSSO_2CH_3$, DMF.

Fig. 5

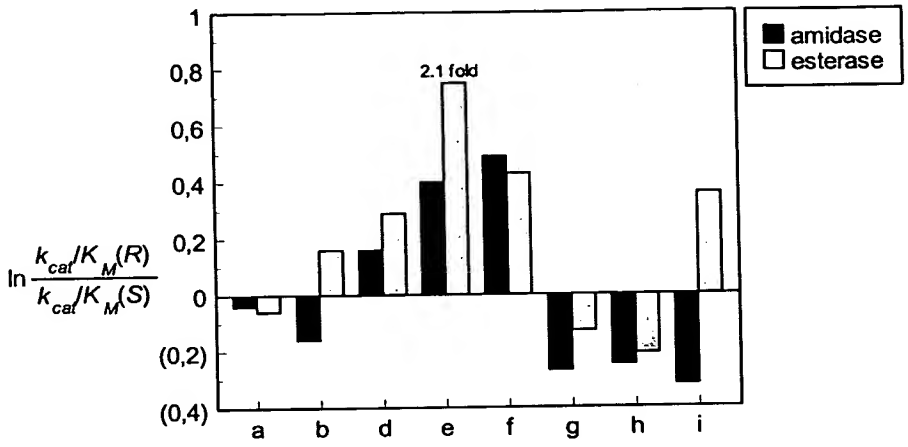

amidase
esterase
2.1 fold
1
0,8
0,6
0,4
0,2
0
(0,2)
(0,4)
a
b
d
e
f
g
h
i
$\ln \frac{k_{cat}/K_M(R)}{k_{cat}/K_M(S)}$

Fig. 6A

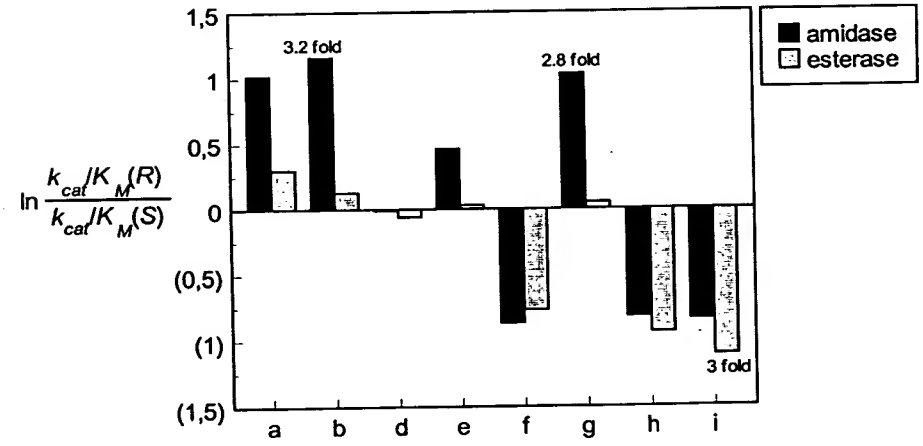

amidase
esterase
3.2 fold
2.8 fold
3 fold
1,5
1
0,5
0
(0,5)
(1)
(1,5)
a
b
d
e
f
g
h
i
$\ln \frac{k_{cat}/K_M(R)}{k_{cat}/K_M(S)}$

Fig. 6B

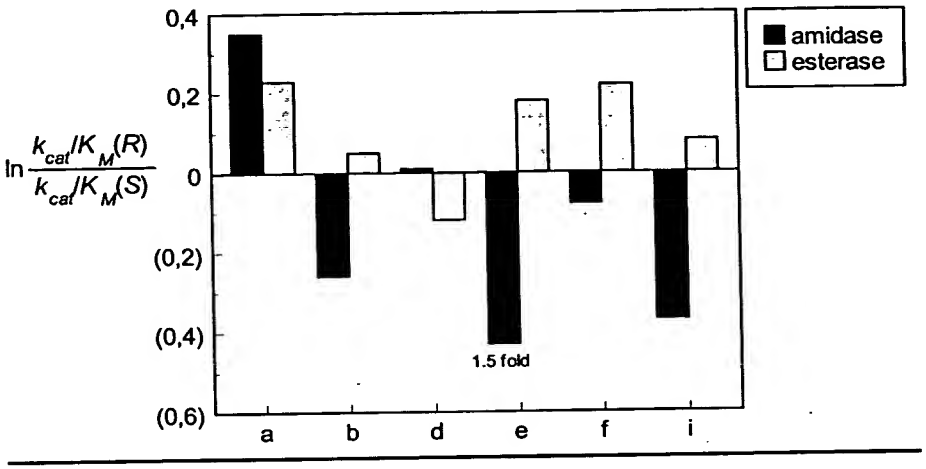

0,4
0,2
0
(0,2)
(0,4)
(0,6)
$\ln \frac{k_{cat}/K_M(R)}{k_{cat}/K_M(S)}$
amidase
esterase
1.5 fold
a
b
d
e
f
i

Fig. 6C

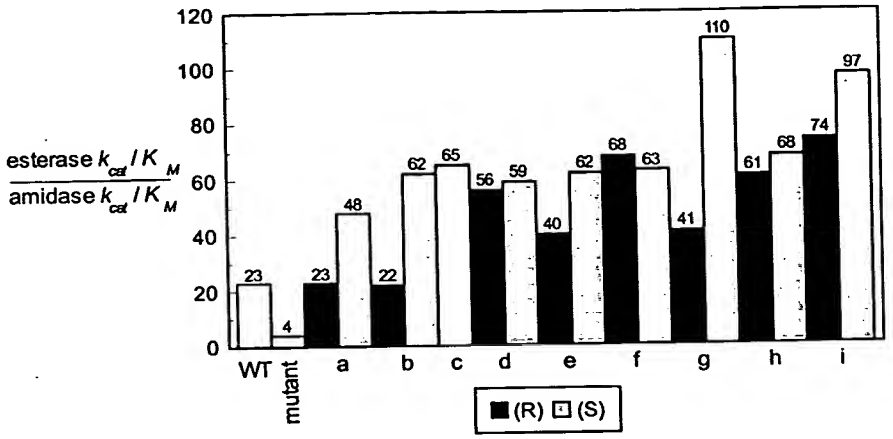

esterase k_{cat}/K_M
amidase k_{cat}/K_M
120
100
80
60
40
20
0
23
4
23
48
22
62
65
56
59
40
62
68
63
41
110
61
68
74
97
WT
mutant
a
b
c
d
e
f
g
h
i
(R) (S)

Fig. 7A

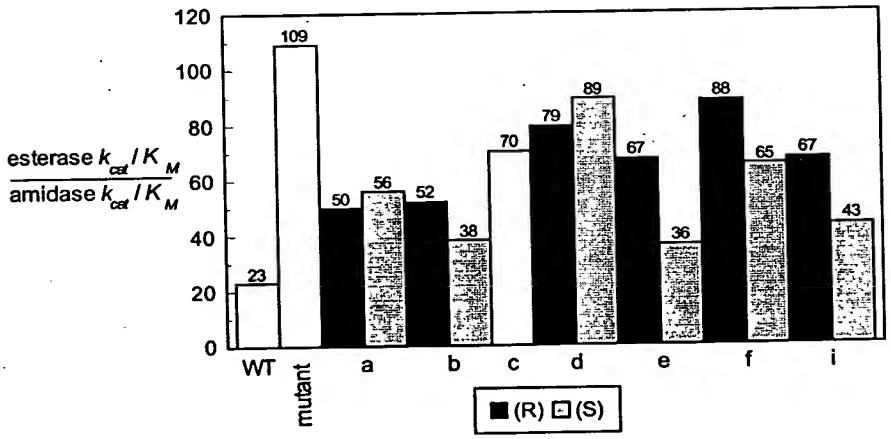

esterase k_{cat}/K_M
amidase k_{cat}/K_M
120
100
80
60
40
20
0
23
109
50
56
52
38
70
79
89
67
36
88
65
67
43
WT
mutant
a
b
c
d
e
f
i
(R) (S)

Fig. 7B

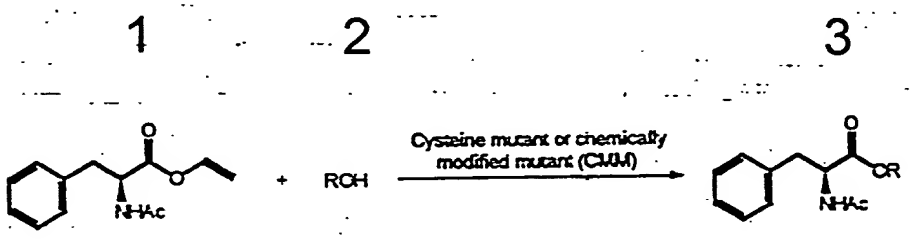

1
2
3
NHAc
+ ROH
Cysteine mutant or chemically modified mutant (CMM)
OR
NHAc

Fig. 8